Electronic Supplementary Information

Ultrastable Zinc-Based Organic Framework as a Recyclable Luminescence Probe for the Methylmalonic Acid Detection

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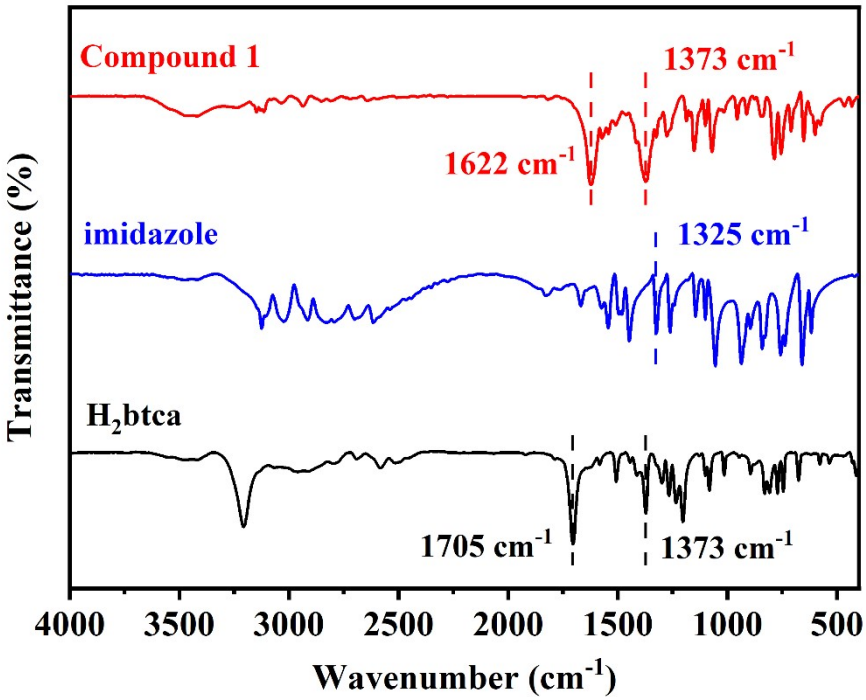

Fig. S1 The FT-IR spectra of compound **1** and ligands. (H_2btca and imidazole). Black: H_2btca; Blue: imidazole; Red: compound **1**.

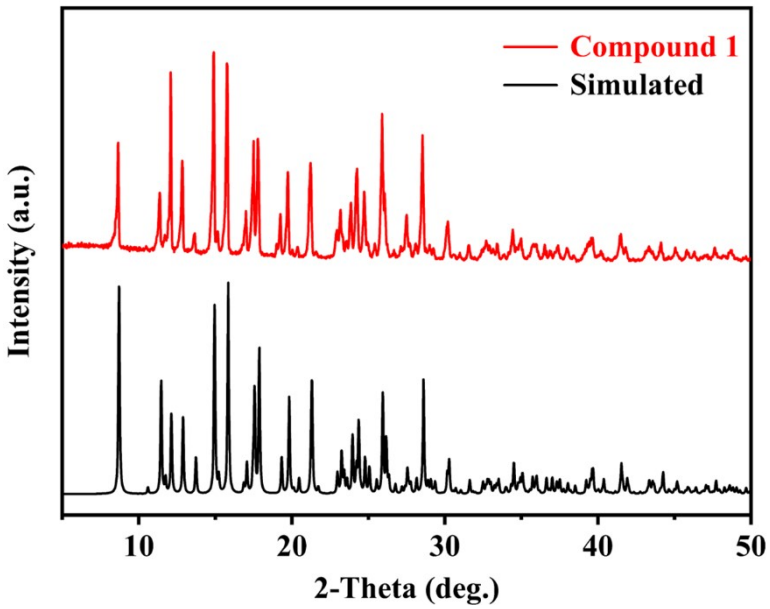

Fig. S2 The PXRD patterns of compound **1** and the simulated ones from Mercury.

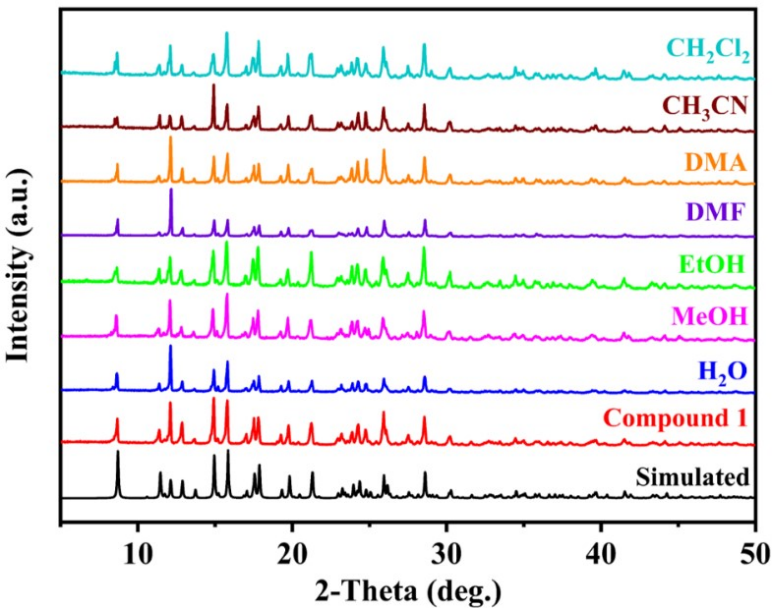

Fig. S3 The PXRD patterns for compound **1** immersing in common solvents (H_2O, N, N'-dimethylformamide (DMF), N, N'-dimethylacetamide (DMA), methanol, ethanol, acetonitrile and dichloromethane) for 12 h.

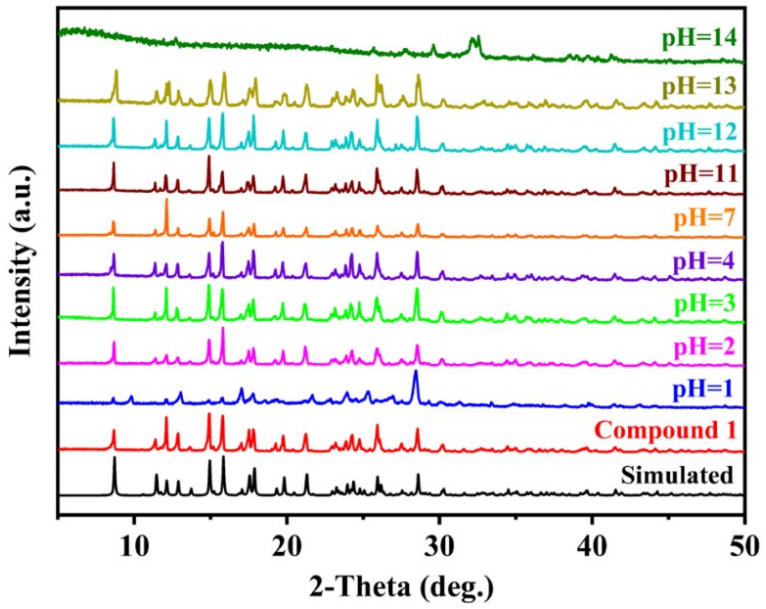

Fig. S4 The PXRD patterns for compound **1** in various acid/base solutions with pH range from 1.0 to 14.0 for 12 h.

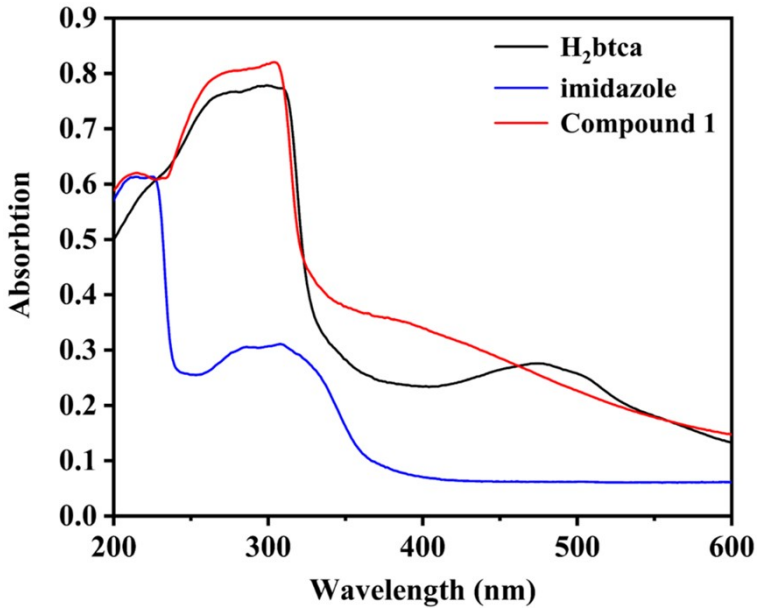

Fig. S5 The solid-state UV spectra for compound **1** and ligands (H_2btca and imidazole). Black: H_2btca; Blue: imidazole; Red: compound **1**.

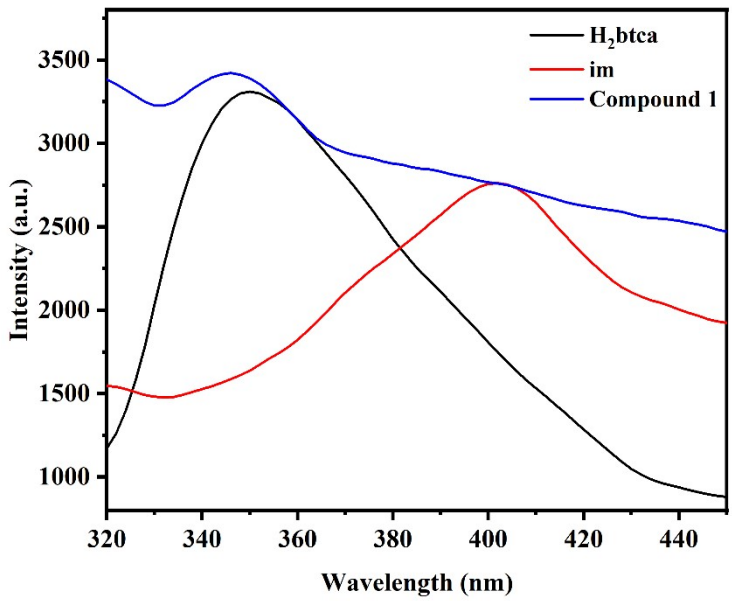

Fig. S6 The solid-state photoluminescence spectrum for compound **1** and ligands (λ_{ex} = 290 nm). Black: H_2btca; Red: imidazole; Blue: compound **1**.

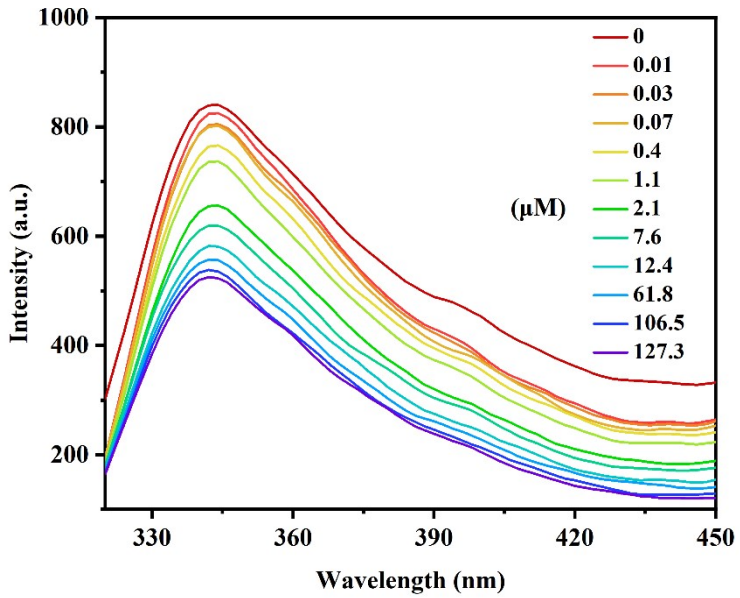

Fig. S7 Fluorescence emission spectra of H_2btca after adding different concentrations of MMA solutions. (λ_{ex} = 280 nm).

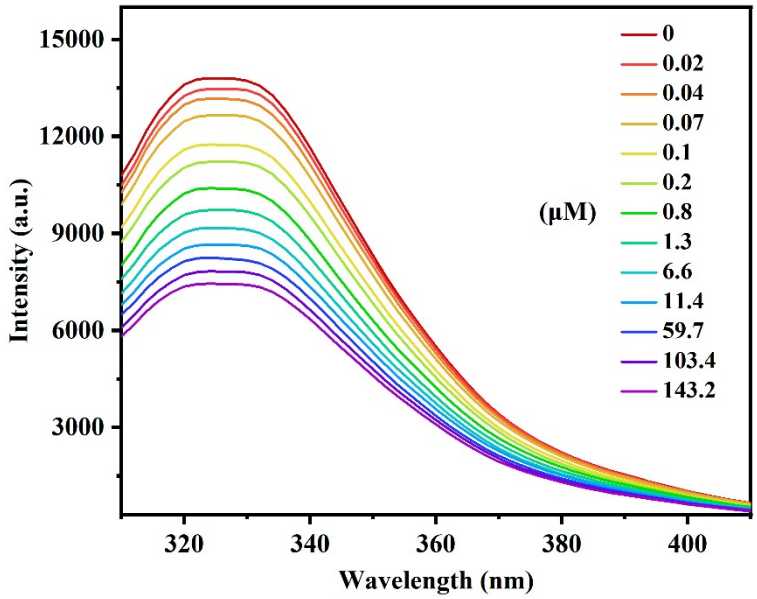

Fig. S8 Fluorescence emission spectra of imidazole after adding different concentrations of MMA solutions. (λ_{ex} = 280 nm).

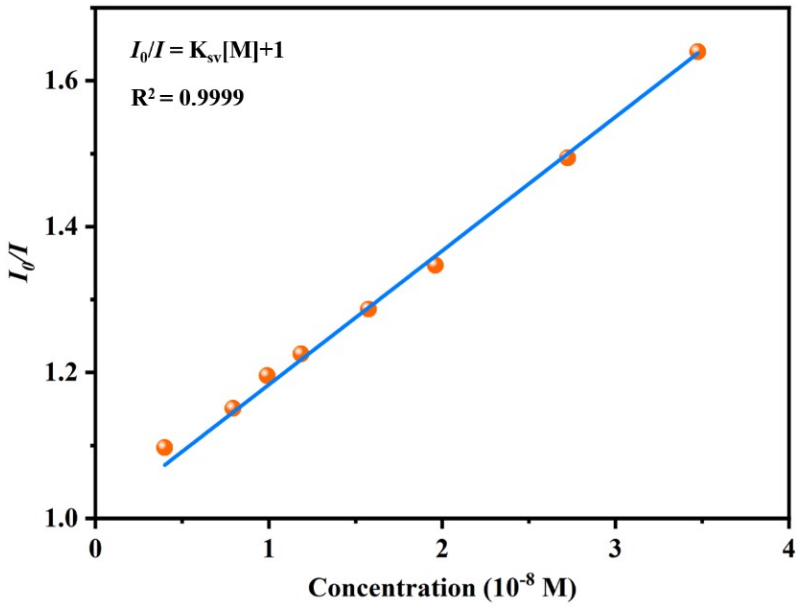

Fig. S9 The luminescence intensity *vs*. methylmalonic acid (MMA) concentration plots (I_0 and I represent the luminescence intensity of compound **1** in aqueous solution before and after adding different concentration of methylmalonic acid, respectively; K_{sv} is the Stern Volmer constant).

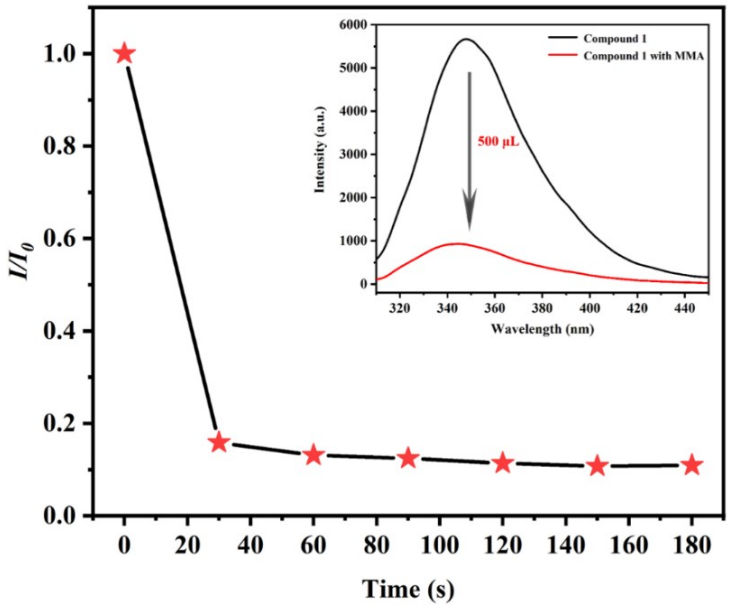

Fig. S10 Quenching efficiency versus response time after adding 1 mg/mL MMA solution to compound **1** (λ_{ex} = 291 nm; λ_{em} = 352 nm. Inset: fluorescence emission spectra of **1** after adding 1 mg/mL MMA).

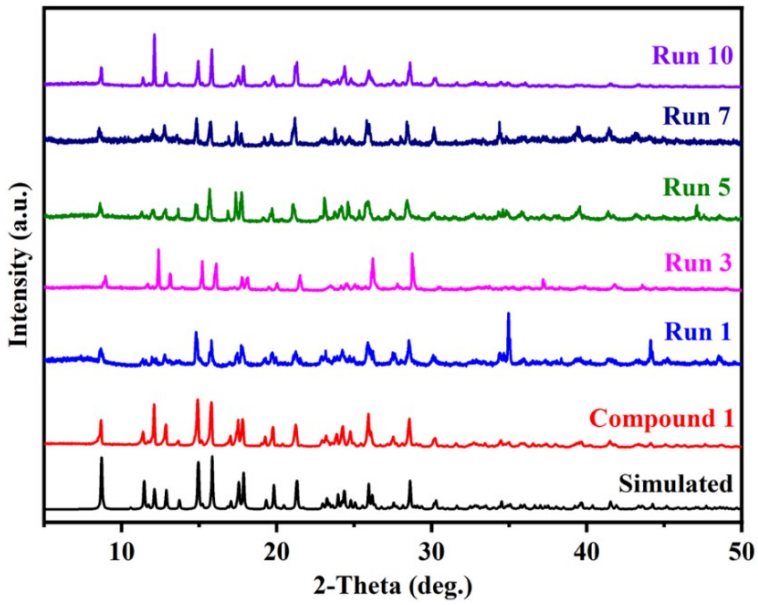

Fig. S11 The PXRD patterns of compound **1** after the recognition cycles for MMA.

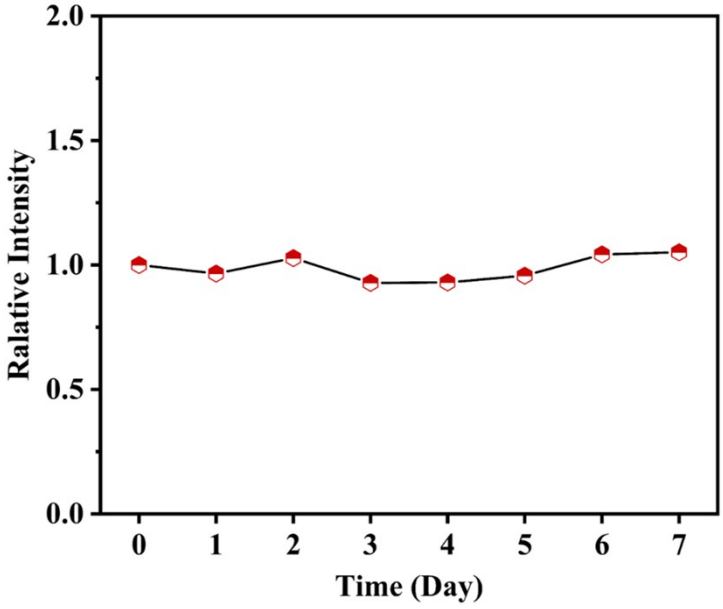

Fig. S12 The fluorescence emission spectra of compound **1** immersed in water for 7 days (λ_{ex} = 291 nm; λ_{em} = 352 nm).

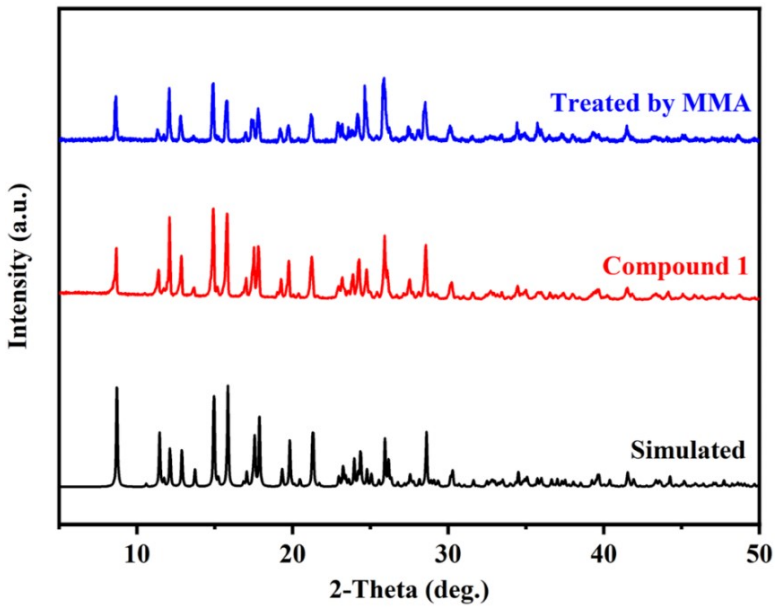

Fig. S13 The PXRD patterns of compound **1** after treated by MMA.

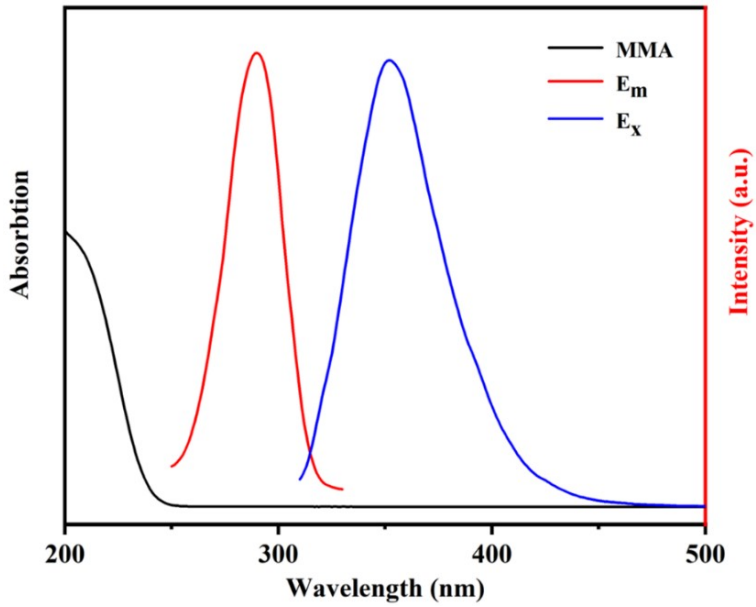

Fig. S14 The comparison of liquid-state UV spectra of MMA (black) and the excitation spectrum (red) and emission spectra (blue) of compound **1**.

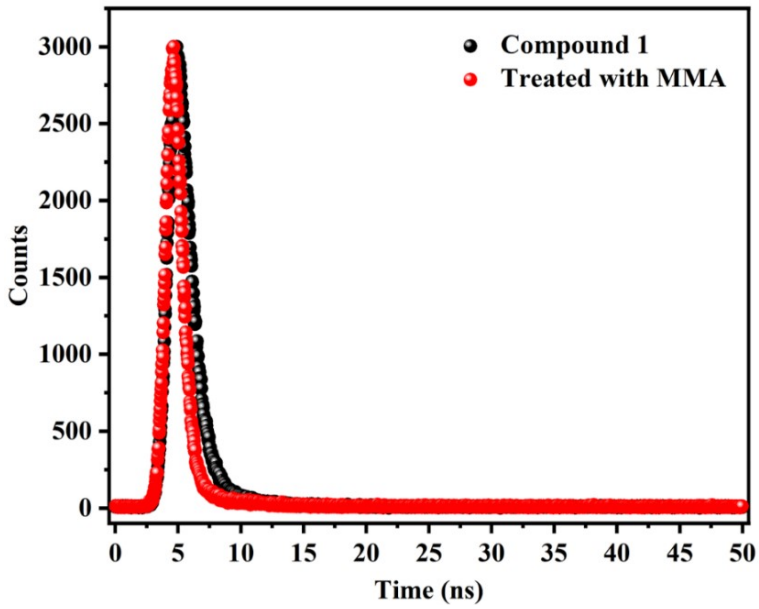

Fig. S15 The time resolved luminescence decay tests of compound **1** (black) and after treated by MMA (red).

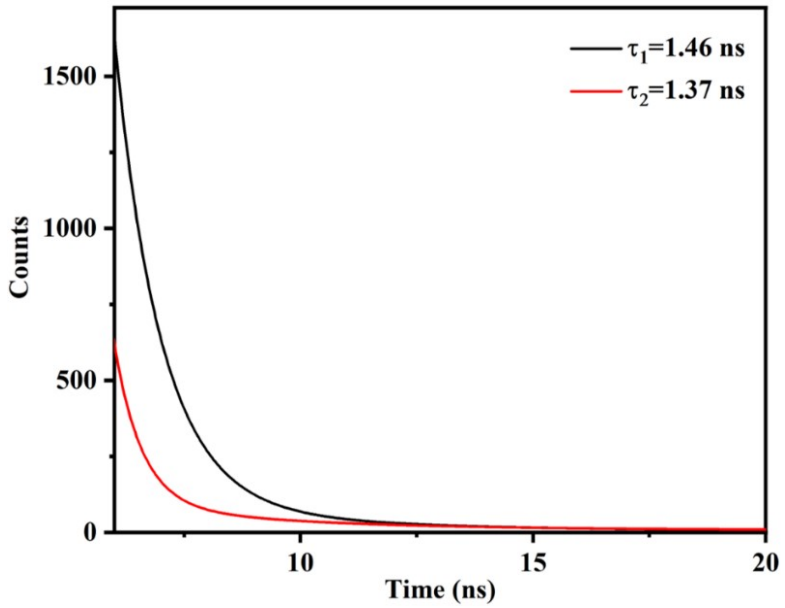

Fig. S16 The time resolved luminescence decay corresponding fitted lines of compound **1** (black) and after treated by MMA (red).

Table S1 Crystal data and structure refinement for compound **1** before and after water treatment for 120 days.

	Compound 1	**After 120 days water treatment (1-H_2O)**
Empirical formula	$C_{24}H_{23}N_{11}O_5Zn_2$	$C_{24}H_{23}N_{11}O_5Zn_2$
Formula weight	676.27	676.27
Crystal system	orthorhombic	orthorhombic
Space group	$Pna2_1$	$Pna2_1$
a(Å)	16.6901(11)	16.5206(2)
b(Å)	8.1097(13)	8.12460(10)
c(Å)	20.2890(12)	20.2605(3)
β(°)	90.00	90.00
Volume(Å^3)	2746.2(5)	2719.43(6)
Z	4	4
ρ_{calc} (g/m^3)	1.636	1.652
μ(mm^{-1})	1.804	2.673
R_{int}	0.0869	0.0405
Goodness-of-fit on F^2	0.954	1.038
Final R indexes [I >=2σ(I)]	R_1 = 0.0741, wR_2 = 0.0987	R_1 = 0.0419, wR_2 = 0.1094
Final R indexes [all data]	R_1 = 0.1486, wR_2 = 0.1185	R_1 = 0.0458, wR_2 = 0.1123

Table S2 Reported chemo-sensors and traditional detection methods for MMA and their detection limits.

Material	Method	LOD	Reference
Ru/Tb@In-MOF	Ratiometric fluorescence sensing	3.8 μg/mL	1
LC-MS	\	2.75 μM	2
GC–FID	\	2.4 μM	3
Anthracene-based fluorescence colorimetric sensor	naked eye colorimetric	1 μM	4
GO/AuNP-g-ATMS-co-AEMA/AA	Electrochemical sensing	0.21 μM	5
Amino acid-functionalized carbon nanodots	Fluorescent sensor array	0.1 μM	6
GC-MS	\	0.025 μM	7
Compound 1	**fluorescence sensing**	**1.7 nM**	**This work**
PdAu-PPy/CFP	Electrochemical sensing	1.32 pM	8
HPLC	\	0.33 pM	9

Table S3 The ICP test for compound **1** after MMA recognition.

Filter liquor	The leakage of Zn^{2+}
After five recycles for sensing MMA	0.097%

Table S4 HOMO and LUMO energies calculated for the ligands and MMA used at B3LYP/6-31G level.

\	HOMO (eV)	LUMO (eV)	Band Gap (eV)
im	-6.140	0.869	7.009
H_2btca	-6.924	-1.976	4.948
MMA	-7.491	-0.247	7.244

Table S5 Recovery test of MMA spiked in urine samples.

Spiked (nM)	Detected (nM)	Recovery (%)	RSD (%, n = 5)
50	49.18	98.4	3.0
100	101.32	101.3	4.5
200	198.02	99.0	2.7

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